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REVISION TO

QUALITY ASSURANCE PROJECT PLAN FOR SOIL SAMPLING AT THE REILLY TAR SITE ST. LOUIS PARK, MINNESOTA

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GCA/TECHNOLOGY DIVISION
Bedford, Massachusetts 01730

REVISION TO

QUALITY ASSURANCE PROJECT PLAN FOR SOIL SAMPLING AT THE
REILLY TAR SITE ST. LOUIS PARK, MINNESOTA

As stated in the original QA Plan, this revision provides detailed information on the physical tests and TOC analyses to be conducted on soil samples. Sections 6.0, 7.0, 8.0 and 11.0 have been revised and the Table of Contents updated to show the current revision of each Section in the Plan.

To update your copy of the QA Project Plan, remove the Table of Contents, Sections 6.0, 7.0, 8.0 and 11.0 and replace them with the enclosed Sections.

RoseMary Ellersick
QA Manager

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6.0 CALIBRATION PROCEDURES AND FREQUENCY

6.1 SAMPLING EQUIPMENT

The equipment to be used is specified in Section 4 of this Plan; no calibration of this equipment is needed. There will be no volume measurements made.

6.2 PHYSICAL TESTING EQUIPMENT

The equipment to be used is specified below; it does not require calibration.

Test	Equipment Used
Vertical column conductivity	Braun-designed test equipment meeting EM 1110-2-1906 specificiations
Horizontal column conductivity	
Particle size	Taylor Soil Series Hydrometer 152 H
Porosity	Volumetric cylinders meeting EM 1110-2-1906 specifications

6.3 OCEANOGRAPHY INTERNATIONAL TOTAL CARBON SYSTEM

The system is calibrated on each analysis day with a 5-point calibration curve run in triplicate. This section addresses the preparation of calibration standards; the ampule sealing and analysis procedures are the same for standards and field samples and are provided in Section 7.2 of this Plan.

6.3.1 Standards

Stock Organic Carbon Solution (1,000 µg C/ml)

Dissolve 2.128g of anhydrous potassium hydrogen phthalate in organic-free water and dilute to 1,000 ml.

Working Standard (10 µg C/ml)

Prepare by diluting 10 ml stock standard (1,000 µg C/ml) to 1 liter with organic-free water.

6.3.2 Procedure for Preparation of Standard Ampules

1. Break open a number of precombusted ampules by snapping at the score line and place in a plastic rack.

2. Add 1 dipper (0.2g) of $K_2S_2O_8$ (potassium persulfate) to each ampule.

3. Prepare a series of ampules containing 0, 10, 20, 30 and 40 g carbon by diluting 0, 1, 2, 3 and 4 ml of the working standard (10 µg C/ml) to 5 ml with organic-free water. Prepare at least three sets of standards with each sample set. Additionally prepare at least three extra blank ampules containing 5 ml of organic-free water.

4. Add 0.25 ml of 6 percent H_3PO_4 to each ampule using a dispenser syringe or automatic pipet.

5. The ampules are now ready for sealing. See Section 7.2, Step VII and following.

Calibration Curve

Average the triplicate intergrator readings of peak area for each standard and graph integration readings vs g of carbon. This graph should be linear in the range of 0 to 40 µg. Read the corresponding µg of carbon for each sample analyzed from the graph.

7.0 ANALYTICAL PROCEDURES

7.1 PHYSICAL MEASUREMENTS

Braun Companies will perform physical measurements on selected Shelby tube corings in accordance with the appropriate standard methodology cited below. A brief summary of each measurement follows.

Measurement Parameter	Method Reference
1. Vertical column conductivity	1. EM 1110-2-1906,[1] pp. VII-13-VII-27
2. Horizontal column conductivity	2. EM 1110-2-1906,[1] pp. VII-13-VII-27
3. Particle size	3. ASTM Methods D422, D1140[2]
4. Porosity	4. EM 1110-2-1906,[1] pp. II-1-II-13

7.1.1 Vertical Column Conductivity Measurements

The conductivity measurements will be conducted on undisturbed samples from Shelby tubes. For the vertical column measurements, a representative sample will be cut from the total Shelby tube sample and placed in a triaxial apparatus for conduct of the test. It has been our experience that it is necessary to place the samples in a rubber membrane with confining pressure to limit leakage of water down the side of the sample. Too often, when running the samples directly in the Shelby tube, a leak develops which distorts the permeability. Because any sample tested in this manner will be cohesive, a falling head permeameter test will be used. This procedure is in accordance with that specified in Manual EM 1110-2-1906,[1] pages VII-13 to VII-27. Measurements will be made to 2 $\pm$ 0.1 centimeter, with results accurate to $\pm 1 \times 10^{1}$ cm/sec. The Peremability Test Data Sheet shown in Figure 7-1 will be used to record data.

7.1.2 Horizontal Column Conductivity Measurements

The horizontal conductivity measurement will be conducted on undisturbed samples cut from Shelby tube samples. It will be necessary to cross section a representative sample and trim it to fit into a triaxial test

PERMEABILITY TEST DATA SHEET

Project: _____

_____

Sample Identification/Location: _____

_____

Specification: _____

Submitted By: _____ **Date Submitted:** _____ **Received By:** _____

Soil Classification: _____

Standard (Modified) Proctor: **Maximum Density** _____ pcf

Optimum Moisture _____ %

Density of Sample: _____ pcf, **% Compaction:** _____

Diameter of Sample, D _____ **Length of Sample, L** _____ **Volume** _____

Area of Sample, A _____ **Dia. of Standpipe, d** _____ **Area, a** _____

Moisture:	At Rec'd.	At end of test	Molding Moisture		Molding Weight	
Wt. of wet Soil + tare			Wt. of wet Soil		Volume	
Wt. of dry Soil + tare			Moisture Content		Dry Density	
Wt. of water			Wt. of dry Soil		Dry Wt.	
Wt. of tare			Optimum moisture		Opt. Moist.	
Wt. of dry Soil			Moisture Factor		Wet Wt.	
Moisture Content			Moisture to add			

Date & Time Start Soaking _____ **Date & Time Start Rdgs.** _____

$k = \frac{c}{t} \log {}^{h_1}/_{h_2}$ $c = 2.3\ a\ L/A =$

Date	Time	Elapsed time, t (sec)	Height of water, h_i (cm)	${}^{h_1}/_{h_2}$	$\log_{10} {}^{h_1}/_{h_2}$	${}^{c}/_{t}$	k, cm/sec

Figure 7-1. Permeability Test Data Sheet.

apparatus. The test will be run with the sample in an impervious membrane subjected to confining pressure to reduce the potential for leakage along the side of the sample. Because any sample tested in this fashion will be cohesive, a falling head permeameter test will be utilized. With the exception of sample preparation, this procedure and tolerances will be the same as those stated in the Vertical Column Conductivity Measurements. Data will be recorded on the Permeability Test Data Sheet.

7.1.3 Particle Size Analysis

The particle size analyses will be conducted in accordance with ASTM D422 and D1140.[2] This provides both the mechanical and hydrometer analysis. The specific gravity will be assumed, based on our extensive experience with the soils in the area. The lower detection limit for grain size distribution is 0.0014 mm for a 24 hour test. Data sheets are shown in Figures 7-2 and 7-3.

7.1.4 Porosity Determination

The porosity of a sample will be determined by measuring the in-place density of undisturbed samples from Shelby tubes. The porosity will then be calculated from the dry density, using an assumed specific gravity typical for soils in the area having a similar geological origin. Figure 7-4 presents the data sheet that will be used.

7.2 TOC ANALYSIS

Soil samples will be analyzed for TOC using an Oceanography International Total Carbon System. A published standard method for TOC analysis of soils is not yet available; EPA Method 415.1[3] is cited as a reference for general background on the analysis. The step-by-step analytical procedure in use in the subcontractor laboratory is provided here even though it duplicates material provided in other sections of this QA Plan. This procedure provides the analyst with calibration, maintenance and troubleshooting information in a readily available fashion.

PARTICLE SIZE DATA SHEET
ASTM D422-63

Project_____ Boring _____

TIME	ELASPED TIME, MIN	TEMP °C	HYD RDG	CORR RDG, R	EFF DEPTH, L	L/T	$\sqrt{L/T}$	K	$D = K\sqrt{L/T}$	$\frac{R}{w} = \frac{P_a}{w} \times 100$
	1									
	2									
	5									
	15									
	30									
	60									
	250									
	1440									

SIEVE ANALYSIS

Sieve Size	Wt. Retained	% Retained	% Passing
2"*			
1 1/2"			
1"			
3/4"			
5/8"			
1/2"			
3/8"			
#4			
#10			
40			
100			
200			
TOTAL SAMPLE WT.			

*Include larger sizes if aplicable.

MOISTURE DETERMINATION

Wet wt. _____
Dry wt. _____
Wt. water _____
m.c. _____

BY: _____

Figure 7-2. Particle Size Analysis Data Sheets.

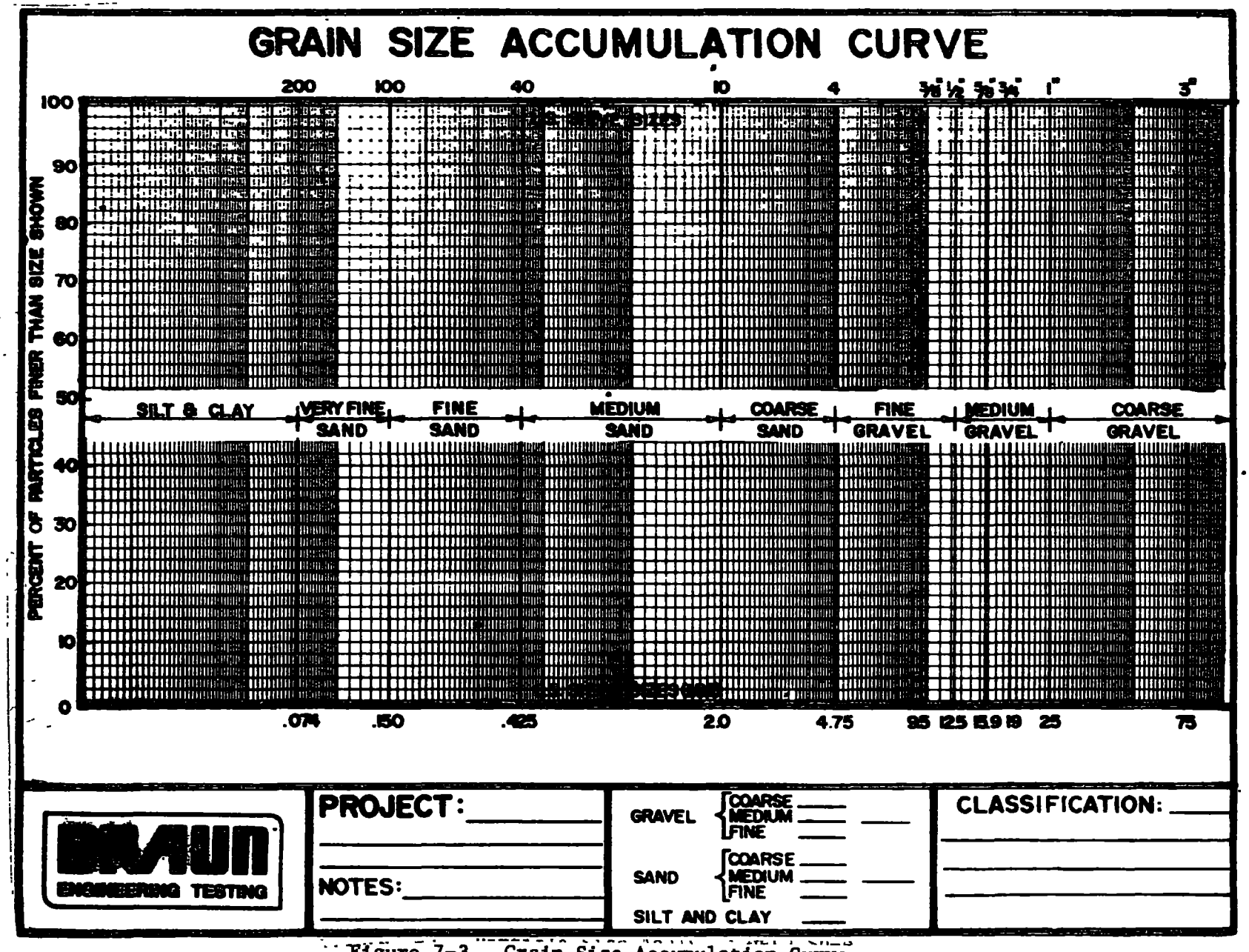

Figure 7-3. Grain Size Accumulation Curve.

WATER CONTENT-DRY DENSITY

WATER CONTENT

BORING NO	
SAMPLE NO OR TW NO	
DEPTH	
CONTAINER NO. (CUP)	
WT OF CUP + WET SOIL	
WT OF CUP + DRY SOIL	
WT OF CUP	
WT OF DRY SOIL	
WT OF WATER	
WATER CONTENT %	

DRY DENSITY

HEIGHT cm	
DIAMETER cm	
Area = diameter^2 x .7854	
VOLUME OF SOIL = area x height	
BULK G = WT DRY SOIL ÷ VOL.	
DRY DENSITY = D_D D_D = G(62.4)	
WET DENSITY	

BRAUN
ENGINEERING TESTING

PROJECT

SOIL DESCRIPTION

TEST BY	DATE TESTED	DATE WEIGHED	JOB NO

Figure 7-4. Porosity Determination Data Sheet.

TOTAL ORGANIC CARBON
(Ampule Method)

I. PRINCIPLE

A known quantity of water or sediment sample is placed in an ampule containing dilute phosphoric acid and potassium persulfate. This solution is purged with oxygen to remove inorganic carbon as CO_2 and flame sealed. The ampules are then subjected to autoclaving where all organic carbon is converted to carbon dioxide. The gases in the ampule are swept through a non-dispersive IR where the CO_2 concentration is determined. The concentration of CO_2 is directly proportional to the amount of organic carbon present in the sample.

II. APPARATUS

1) Oceanography International Total Carbon System including:

   a) Purge and Seal Unit,

   b) Ampule Analyzing Unit,

   c) Direct Injection Module.

2) Autoclave or Pressure Cooker.

3) 10 ml borosilicate glass ampules (precombusted) or combust by heating @ 550°C for four hours.

4) Ampule racks for autoclaving.

5) dipper for $K_2S_2O_8$.

III. REAGENTS

1) Potassium Persulfate ($K_2S_2O_8$) granular.

2) 6% Phosphoric Acid (H_3PO_4)

   Add 60 ml of 85% H_3PO_4 carefully to 500 ml of organic free water. Dilute to 1,000 ml.

3) Organic Free Deionized Water

   Store in a borosilicate glass container.

IV. STANDARDS

1) Stock Organic Carbon Solution (1,000 µg C/ml)

   Dissolve 2.128 g of anhydrous potassium hydrogen phthalate in organic free water and dilute to 1,000 ml.

2) Working Standard (10 µg C/ml)

Prepare by diluting 10 ml stock standard (1,000 µg C/ml) to 1 liter with organic free water.

3) Calibration Standards

Prepare a series of ampules containing 0, 10, 20, 30 and 40 µg carbon by diluting 0, 1, 2, 3 and 4 ml of the working standard (10 µg C/ml) to 5 ml with organic free water. Prepare at least 3 sets of standards with each sample set. Additionally prepare at least 3 extra blank ampules containing 5 ml of organic free water.

V. PROCEDURE FOR PREPARATION OF WATER SAMPLES AND STANDARDS

1) Break open a number of precombusted ampules by snapping at the score line and place in a plastic rack.

2) Add 1 dipper (.2 g) of $K_2S_2O_8$ (potassium persulfate) to each ampule.

3) Add an amount of sample (up to 5 ml) expected to contain between 20 and 40 µg of carbon to a series of ampules. Normally a series of three ampules per sample is used to bracket expected concentrations and as a safeguard for ampule breakage.

4) Prepare blanks and standards in a similar manner.

5) Dilute all samples and blanks to 5.0 ml with organic free water.

6) Add .25 ml of 6% H_3PO_4 to each ampule using a dispensor syringe or automatic pipet.

7) The ampules are now ready for sealing.

VI. PROCEDURE FOR PREPARATION OF SOLID AND SEDIMENT SAMPLES

1) Sediment sample must be dried (105°C) and homogenized to a fine powder (ball mill or grinder).

2) Weigh an amount of sediment to the nearest .01 mg using the Cahn 25 Balance.

3) Choose the sample size to approximate 30 µg carbon in the sample based upon the expected percentage of organic carbon. Use the following table as a guide.

Estimated Percent Carbon	Sample Size (mg)
0.1%	30.0
1.0%	3.0
10.0%	0.30

4) Weigh the sample and transfer to an ampule using the following procedure.

   a) Place a small powder paper on pan B and tare the balance.

   b) Place an amount of sample on the weighing paper, reweigh and record weight.

   c) Transfer this sample to an ampule using a disposable pasteur pipet tip as a funnel.

   d) After transfer reweigh the powder paper and subtract the weight of any residual sediment from the weight recorded in Step (b). This is the actual amount of sample transferred to the ampule.

   e) Prepare triplicate ampules for each sample.

5) Add 1.0 ml, 6% v/v phosphoric acid solution to ampule.

6) Add 2.0 ml distilled water. (Inject water into ampule in a manner so that sides of the ampule are washed and all the sample and acid are carried to the bottom.)

7) Cover ampules with aluminum foil and let stand for 30 minutes. (This allows adequate time for the HCO_3^- and $CO_2^= \rightarrow CO_2 \uparrow$ conversion.)

8) Add 0.2 g $K_2S_2O_8$ to ampule with dipper measure.

9) Add 2.0 ml distilled water to ampule. (Inject water in a manner such that the $K_2S_2O_8$ is washed to the bottom of the ampule.)

10) Ampules are now ready for purging and sealing.

VII. OPERATION OF THE AMPULE PURGING AND SEALING UNIT

General Description

The Ampule Purging and Sealing Unit purges glass ampules of inorganic carbon components with purified oxygen flowing at a rate of approximately 80 ml/min. The oxygen is purified by passing through an 8-inch cupric oxide catalyst tube heated electrically to 475°C by a 192-watt element. Sealing of the ampule is accomplished with an oxygen-propane microburner. The neck of the ampule is held by a clamping assembly and the lower portion of the ampule is twisted manually after the neck of the ampule bcomes molten. "Purge cones" prevent introduction of carbon dioxide contamination from the microburner during the sealing operation.

Operation

NOTE: SAFETY GLASSES MUST BE WORN DURING THIS OPERATION!

1) Connect the sealing unit to a cylinder of commercial oxygen fitted with a pressure reducing regulator with the length of 1/4" O.D. plastic tubing provided.

2) Open main valve of the oxygen cylinder and adjust pressure regulator to deliver at a pressure of 22 p.s.i.

3) Turn on catalyst heater by means of on/off switch (Figure 1-J). Adjust input voltage on the variac to 55 volts to give a constant temperature of 450°C-500°C as indicated on the pyrometer (Figure 1). CAUTION: Maximum temperature for the heating element is 525°C.

4) Allow at least 15 minutes for unit to purge at 450°C before placing ampules in purging position (Figure 1).

5) Place purge cone on each ampule to be sealed (Figure 1-A). For best precision, cones must be cleaned with distilled water before each set of samples.

6) Place ampule into purging position (Figure 1) and insert a glass purge tube through purge cone to the bottom of the ampule (Figure 1-B). Purge for six minutes, 10 ml size (five minutes for 5 ml sample water) to remove inorganic carbon components. Replace purge tubes with clean ones before each use. Store purge tubes and purge cones in container provided on unit for convenience (Figure 1-C).

7) Ignite the microburner (Figure 1-D). See "Lighting Sequence." The microburner has been adjusted to give the correct heat for sealing prior to shipping. Minor heat adjustments may be necessary for different operators. The valves to the right marked MICROBURNER ADJUST (Figure 1-E) are for fine adjustment; the toggle valves marked PROPANE and OXYGEN (Figure 1-F) serve as On/Off valves. Once the proper flame has been attained, the MICROBURNER ADJUST valves should not be turned. Turn the flame on or off with the toggle valves on the left only.

Lighting Sequence

a) Open propane tank main valve on propane cylinder.

b) Open PROPANE toggle valve.

c) Ignite propane gas at microburner. CAUTION: Propane may flare; keep well away when lighting.

d) Wait 10 to 15 seconds for propane gas flame to reach maximum intensity. (This waiting period is necessary due to the very small gas flow through the propane gas regulator. Should the oxygen be turned on prior to the time the propane flame reaches its maximum intensity, the mixture of gases will be oxygen-rich, causing an explosive mixture instead of a burning mixture.)

e) Open OXYGEN toggle valve slowly.

f) Flame should be approximately 1/16" long. Flame tips should be neutral in appearance. Excess oxygen will cause the flame to "pop" with a considerable percussion. Be prepared, as it can be alarming!

8) Place an ampule that has been purged of inorganic carbon components (six minutes) into the clamping assembly (Figure 1-H, 2). The glass purge tube should be placed in the rubber tube holder during this operation (Figure 4-A).

9) Press ampule holding lever with thumb and place the base of the ampule into position (Figure 2).

10) Raise purge tube and press into purge tube holding assembly (Figure 4-A).

NOTE: Bottom of purge tube should be even with underside of clamping assembly, but still lower than apex of purge cone.

11) Swing the microburner into place and seal the ampule (Figure 3).

NOTE: Only several seconds are necessary for the thin glass neck of the ampule to reach the molten state. When the molten state has been rached the ampule is pulled down approximately 3/8". This movement decreases the diameter of the neck. The ampule is then twisted rapidly for several turns without raising or lowering the ampule. The twisting motion is necessary to seal off any capillary that might otherwise be formed. Practice this procedure with ampules filled with water until a good seal can be formed each time. Care must be taken not to allow the partially sealed ampule to be raised up into the flame as gas expansion within the ampule will cause a thin glass bubble to form at the tip. If the ampule is pulled down too far the seal will be a long, sharp, easily broken one. On the other hand, if the ampule top is too thick, difficulty will be experienced in breaking the top of the ampule during analysis. Several of the practice ampules should be placed in the ampule analyzing unit and checked for ease of breaking.

12) Remove the microburner from the sealing position as soon as the ampule has been sealed. This prevents overheating of the clamping assembly.

13) Place the glass purge tube and purge cone in another ampule, and place in purging position.

14) Remove the sealed ampule from the holder.

15) Open the clamping assembly and permit the hot ampule tip to drop in a glass beaker.

Turning Off the Sealing Unit

a) Slowly close OXYGEN toggle valve.

b) Wait until a pure propane flame appears.

c) Close PROPANE toggle valve.

d) Close main valve on propane cylinder.

e) Close main valve of oxygen cylinder.

f) Turn off catalyst heater.

Hints to Obtain Best Results

a) Purge and seal first those ampules containing samples of lowest carbon concentation.

b) Do not allow smoking when preparing and sealing ampules.

c) Always cover ampules with a sheet of thin aluminum foil during preparation and prior to sealing in order to prevent dust particles from contaminating them.

d) Use glass-stoppered bottles for storage of sample water, phosphoric acid solution, and potassium persulfate.

e) Always use clean purge tubes and purge cones.

f) Clean glass purge tubes and purge cones by drawing boiling distilled water through them with suction. Purge cones fit into 3/16" I.D. Tygon tubing attached to the vacuum source. Place a rubber seal (similar to the one used to seal the stainless steel purge tube in the ampule crushing assembly) in the 3/16" Tygon tubing to reduce the opening to fit the glass tube. Wipe the outside of the tube with a clean damp tissue first and then draw hot water through the tube. Handle only the end of the tube that was placed into the seal. Place clean tube into the screwcap storage vial until used. Do not attempt to completely dry the tube. Do not smoke while cleaning the tubes or cones.

g) The ampule sealing unit should be placed such that the operator is looking up and under the microburner when sealing an ampule. This position makes it much easier to determine when the molten state has been reached and thus when to lower the ampule 3/8" and begin to twist the ampule.

h) Use of glass blower's glasses to remove the sodium spectrum from the flame allows one to better see when the molten state has been reached.

VIII. SAMPLE DIGESTION PROCEDURE

After sealing, as described in the preceding section, the conversion of organic matter to carbon dioxide is accomplished at elevated temperatures. The quantitative oxidation of organic matter by persulfate may be achieved by placing the

sealed ampules in a standard laboratory autoclave (pressure cooker) set at 130°C for a period of four hours, minimum time.

The following steps are required in using the autoclave:

1) Place ampules in the racks provided with tips pointing down. Make a record of the corresponding rack position number to the identifying ampule marking. This is necessary as the marking on an ampule is removed by the high temperature water contained in the pressure vessel.

2) Place the metal disc over the ampules and secure metal disc with knurled screw. This prevents ampules from floating out of position.

3) Place the filled racks into the autoclave (pressure cooker).

4) Turn on the autoclave and after initial warmup adjust to 130°C.

5) Let samples digest for 4 hours.

6) After 4 hours turn off autoclave and allow pressure to slowly decrease. Rapid decrease in pressure will cause the ampules to explode.

7) Remove ampules when cool. Inspect for leakage.

8) Autoclave (pressure cooker) should be cleaned frequently when breakage occurs to remove H_3PO_4 and $K_2S_2O_8$ which will corrode interior.

IX. AMPULE ANALYZING UNIT DESCRIPTION

This unit contains a non-dispersive infrared analyzer and is used to analyze the contents of glass ampules for the concentration of carbon dioxide resulting from the wet oxidation of organic matter, the high temperature oxidation of organic carbon in conjunction with the Direct Injection Module, and the inorganic carbon resulting from the acidification of bicarbonates and carbonates in solution. Operation of the IR analyzer is covered by the IR analyzer instruction manual. The unit allows ampules to be analyzed easily without introducing atmospheric carbon dioxide and to remove water vapor from the carrier gas stream prior to reaching the IR analyzer. This unit also removes water vapor from the oxygen carrier gas stream from the Direct Injection Module. Up to 150 ampules can be analyzed in a day.

Prior to use, fill the drying tubes (Figure 5) with granular magnesium perchlorate. The first tube on the left is a water vapor trap to remove gross amounts of water vapor (Figure 5-A). This tube is not packed with magnesium perchlorate. The second tube is the primary drying tube filled with magnesium perchlorate (Figure 5-C). The flow of gas through this tube is from bottom to top. The third tube (Figure 5-D) on the front and the long drying tube inside the cabinet are mainly to insure that no water vapor is transmitted in the carrier gas stream to the IR analyzer. Glass wool plugs are placed in the ends of all tubes except in the water removal tube. The tubes should be filled with magnesium perchlorate, sieved to 40 mesh, and tapped only gently in order not to restrict the gas flow any more than necessary.

A glass wool filter has been placed at the outlet of the ampule breaking assembly (Figure 7-A) to prevent small particles of glass from clogging the plastic gas line leading from the assembly to the first water removal tube (Figure 5-A). Replace the glass wool plug when necessary.

The ampule breaking assembly should be taken apart (Figure 8) when glass ampules are being analyzed and all particles of glass purged out with water after breaking about thirty ampules. Small particles of glass will tend to blow up into the stainless steel purge tube causing a reduced flow. This restriction is cleared by removing the plastic gas line from the purging tube (Figure 6-1) and pusning a length of steel wire through the tube. A build-up of glass particles within the ampule breaking assembly tends to bind the free movement of the stainless steel purge tube. Usually several up-and-down movements of the purge tube will remedy this situation. The silicone rubber seal which seals the purge tube within the ampule cutting plunger (Appendix C) should be replaced after several hundred ampules have been analyzed or before if the center hole in the seal becomes enlarged. Silicone grease should be used to lubricate the purge tube whenever necessary.

The primary drying tube (Figure 5-C) will need replacing often. Usually the lower inch of magnesium perchlorate becomes exhausted, indicated by changing from dry granular to a semi-liquid state. Whenever a reduction in the carrier gas flow rate is noted, this drying tube should be checked first as the probable cause of the reduced flow rate. (Check the stainless steel purge tube for the restriction due to particles of glass within the tube.)

A. Connecting Ampule Analyzing Unit to Gas Supplies

1) Connect unit to commercial nitrogen (zero gas) cylinder regulators with 1/4" O.D. polyethylene tubing (Figure 9) supplied with the unit.

2) Check that ZERO GAS (Figure 6-D) and SPAN GAS (Figure 6-G) toggle valves are "OFF" (handle pointing down). SPAN GAS should always be "OFF."

3) Adjust delivery pressure to 12 p.s.i. at the N_2 cylinder regulator.

X. DAILY OPERATION PROCEDURE

1) The IR analyzer should be left on at all times to eliminate the need for warm-up.

2) Place the standardization vial in the ampule breaking assembly or place an ampule in the assembly. (Use plastic adaptor and gum rubber gas seal (Figure 7).

3) Position the two-way valve (Figure 6-B) to "Out-to-Analyze" position so that IR carrier gas flows through the ampule breaking assembly.

4) Open ZERO GAS (Nitrogen) toggle valve (handle straight out).

5) Place FLOW toggle valve (Figure 6-C) in open position (handle straight out).

6) Adjust IR RATE valve (Figure 6-E) to give a flow rate of 200 ml/min. (reading of 13), indicated by the rotometer (Figure 6-A).

7) Allow system to purge, then zero the IR analyzer meter to read zero.

8) Pull out the IR analyzer and connect the 43 ohm resistor to ground and the capacitor post.

9) Adjust the SPAN control on the IR analyzer to give a reading of 90 on the IR meter (Figure 6-H).

NOTE: The SPAN control of the IR analyzer is shown in Figure 6-J.

10) Remove the resistor and re-set at zero.

11) Repeat steps 9 and 10 until the meter reads zero without the resistor and 90 with it without the need for adjustment.

12) If these conditions cannot be met, the IR may need re-alignment. Refer to pages 2-7 of the IR manual for this procedure.

13) Electronic Integrator Adjustment:

Four controls are used to operate the electronic integrator. The ON-OFF switch supplies power to the integrator assembly. the LAMP TEST push switch causes all segments of each digit to illuminate when the switch is pushed. The AREA CLEAR switch, when momentarily pressed in the MANUAL position, clears the integrator and puts all digits to zero. The ZERO BASELINE is a fine adjustment to make the integrator give zero integration. All other controls on the integrator panel are for the electronic printer and are not used for normal integrator operation.

The electronic integrator is placed in operation by placing the power switch to the ON position. All digits should be illuminated and show some number. Press the LAMP TEST switch to check illumination of all segments of each digit. Re-zero the IR analyzer if necessary with the IR ZERO control so that the meter reads zero. Adjust the integrator ZERO BASELINE control clockwise until integration slowly occurs. If there is not sufficient adjustment with the integrator ZERO BASELINE control, then re-adjust the IR analyzer ZERO control slightly clockwise until integration begins. Then, slowly turn the ZERO BASELINE control counter-clockwise until integration just stops. This adjustment is a delicate one and must be carefully made in order to achieve the maximum precision of the integrator. Basically, consider the ZERO adjust of the IR Analyzer to be a <u>coarse</u> adjustment and the integrator ZERO BASELINE control to be a <u>fine</u> adjustment. The range of the integrator ZERO BASELINE control is approximately 2% of a full scale IR Analyzer meter reading.

When zero integration has been achieved, clear the integrator by pressing AREA CLEAR switch to the MANUAL position. The integrator is now ready for use.

XI. <u>OPERATION OF THE UNIT WITH SAMPLE AMPULES</u>

1) Zero and span adjustments have been made. Electronic integrator has been adjusted to give zero integration.

2) Place two-way valve (Figure 6-B) to "IR BY-PASS" or IN position.

3) Place sample ampule in unit (plastic adaptor and gum rubber seal on ampule (Figure 7)).

4) Push the stainless steel purge tube down close to the top of the ampule.

5) Open PURGE RATE valve to give a purging rate of approximately 200 ml/min. (13 on rotometer).

6) Purge for ten seconds.

7) Pull two-way valve (Figure 6-B) to OUT position so that IR analyzer carrier gas flows through the ampule breaking assembly.

8) Check flow rate for 200 ml/min. (13 on rotometer)

9) Stop IR carrier gas by placing FLOW toggle valve to "Off" position.

10) Wait for flow rate to fall to zero on rotometer.

11) Raise purge tube clear of plunger cutters.

12) Break ampule top (Figure 8) and push purge tube to within 1/8" of ampule bottom.

13) Open FLOW valve when rotometer returns to zero flow rate, and check for flow rate of 12.5 to 13.

NOTE: Waiting for a zero flow rate in Steps 10 and 13 has been found to give better precision.

14) Prepare another ampule with plastic adaptor and gum rubber seal for placing in the ampule breaking assembly.

15) Allow gaseous contents of ampule to pass into IR analyzer.

16) Change position of the two-way valve to IN (by-pass) after the carbon dioxide peak has been formed on the meter readout and the meter needle is exactly at the 3% point.

17) Place the next sample in the ampule breaking assembly.

18) Record the electronic integrator reading and zero the integrator after zero integration is noted.

19) Repeat the procedure starting with Step 7. If the two-way valve was changed at the above given points, adequate purging will have taken place.

20) Analyze blanks and standards first to establish working range and suitability of digestion.

XII. IMPORTANT THINGS TO REMEMBER

1) Step 8 is a check for leaks in the system, obstructions in the gas flow system, i.e., small bits of glass in the purging tube and associated gas lines: the settling of exhausted magnesium perchlorate in the primary drying tube.

2) Use several trial ampules at the beginning of a series of ampules. This practice will allow a water vapor equilibrium to be established in the system. If trial ampules are not used, the first several carbon dioxide peaks may be high.

3) Peak area should be used in lieu of peak height for best precision. The electronic integrator will indicate peak areas.

4) Analyze all ampules at the same rate sequence, i.e., two or three minute intervals for best precision.

5) Peak height and peak area change with different flow rates. Flow rate must be kept constant.

6) This is a low pressure system. The slightest obstruction in any of the gas lines will change the flow rate. Changes in flow rate are usually due to:

   a) Primary drying tube exhausted and settled.

   b) Leaky ampule seal, crack in ampule below seal (reason for flow rate check in Step 13).

   c) Small particles of glass lodged in the purge tube.

XIII. CALCULATIONS

Make a graph of integration reading vs. µg of carbon. This graph should be linear in the range of 0-40 µg. Read the corresponding µg of carbon for each sample determined from the graph.

$$\text{mg/l organic carbon} = \frac{\mu g \text{ carbon}}{\text{ml of sample}}$$

REFERENCE

Instruction and Procedures Manual, Oceanography International Corporation, College Station, Texas.

7.3 REFERENCES

1. Engineering and Design Manual EM 1110-2-1906, Laboratory Soils Testing, Department of the Army, Office of the Chief of Engineers, 1970.
2. 1982 Annual Book of ASTM Standards, Part 19, American Society for Testing and Materials, Philadelphia, PA. 1982.
3. Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Cincinnati, OH. 1979.

8.0 DATA REDUCTION, VALIDATION AND REPORTING

8.1 DATA REDUCTION

Braun Companies will use the data reduction and reporting procedures specified in the Laboratory Soils Testing Manual and the ASTM methods cited in Section 7.0 of this Plan for physical test measurement data. TOC results on soil samples will be reported as milligrams TOC/kilogram soil sample.

8.2 DATA VALIDATION

Data validation is the process of filtering data and accepting or rejecting it on the basis of sound criteria. GCA/Technology Division and Braun Companies supervisory and QC personnel will use validation methods and criteria appropriate to the type of data and the purpose of the measurement. Records of all data will be maintained, even that judged to be an "outlying" or spurious value. The persons validating the data will have sufficient knowledge of the technical work to identify questionable values.

GCA's Technical Representative will validate the Drillers logs onsite and initiate any corrective action necessary to obtain complete and correct data. The Braun Companies staff will validate physical testing and TOC analysis results. GCA's Project Manager will review and validate all the field data.

8.3 IDENTIFICATION AND TREATMENT OF OUTLIERS

A data point which deviates markedly from others in its set of measurements may be referred to as an outlier. An outlier may result from an error in the measurement system or technique, or it may be a valid value due to unique circumstances at the time of sampling, analysis, or data collection. A suspected outlier value will be recorded and retained in the data set while it is investigated.

Drillers logs, field and laboratory notebooks will be checked to see if they indicate any unique circumstances which occurred during drilling, sampling or testing. A simple statistical test will be performed on suspected outliers; GCA/Technology Division staff members usually use one or both of the following tests to identify outliers.

Dixon's test for extreme observations[1,2] is an easily computed procedure for determining whether a single very large or very small value is consistent with the remaining data. The one tailed t test for difference[2] may also be used in this case. The calculation formats and tables of critical values given in Reference 2 will be used for these tests. It should be noted that these tests are designed for testing a single value. If more than one outlier is suspected in the same set of data, the statistical sources listed in References 1 through 6 are consulted and the most appropriate test of hypothesis is used.

If the suspect value is statistically identified as an outlier, further investigation will be initiated. The operator, analyst, or data gatherer who worked with the sample will be consulted for his knowledge of the specific sample and his experience with similar samples. This may give an experimental reason for the outlier and a decision can then be made as to whether the outlying value should be kept in the data set.

Further statistical analyses are performed with and without the outlier to determine its effect on the conclusions. In many cases, two data sets will be reported, one including and one excluding the outlier.

8.4 DATA REPORTING SCHEME

The data reporting scheme and key people who will handle the gathering and evaluation of data are shown in Figures 2-1 and 2-2, the Project Organization Charts.

8.5 REFERENCES

1. Dixon, W. J. Processing Data for Outliers, Biometrics, 9(1): 74-89. 1953.
2. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I - Principles, EPA-600/9-76-005, Research Triangle Park, North Carolina. 1976. SEctions C, D, F, H.

3. Handbook for Analytical Quality Control in Water and Wastewater Laboratories, U.S. Environmental Protection Agency Technology Transfer, Cincinnati, Ohio. 1979. Section 6.

4. Industrial Hygiene Service Laboratory Quality Control Manual, Technical Report No. 78, DHEW, PHS, National Institute for Occupational Safety and Health, Cincinnati, Oh. 1974. Section XI.

5. Juran, J. M. Quality Control Handbook, Third Edition, McGraw-Hill, New York. 1974.

6. Freund, J. E. Modern Elementary Statistics, Fourth Edition, Prentice Hall, Inc., Englewood Cliffs, New Jersey. 1973.

11.0 PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES

GCA/Technology Division and Braun Companies follow an orderly program of positive actions to prevent the failure of equipment or instruments during use. This preventive maintenance and careful calibration help to ensure accurate measurements from field and laboratory instruments.

11.1 DRILLING AND SAMPLING EQUIPMENT

The GCA Field Representative will ensure that all drilling and sampling equipment is in proper working condition and is maintained in that condition throughout the performance of this program. Maintenance consists of proper cleaning of the sampling tube and sampler head before each sample is colected (see Section 4.2.2 in this Plan). In addition, the sampling tube edge must be properly sharpened whenever necessary to ensure a smooth edge.

11.2 PHYSICAL TESTING EQUIPMENT

Maintenance of the physical testing equipment consists of proper cleaning of the equipment before each use on samples.

11.3 TOC ANALYSIS SYSTEM

Maintenance of the Oceanography International Total Carbon System is performed as directed in the manufacturer's manual and documented in the maintenance log kept by the instrument. Routine maintenance procedures are listed below for the different parts of the Analyzer.

Purge and Seal Unit

- Clean glass purge tubes and purge cones by drawing boiling distilled water through them with suction. Purge cones fit into 3/16 in. I.D. Tygon tubing attached to the vacuum source. Place a rubber seal (similar to the one used to seal the stainless steel purge tube in the ampule crushing assembly) in the 3/16 in. Tygon tubing to reduce the opening to fit the glass tube. Wipe the outside of the tube with a clean damp tissue first and then draw hot water through the tube. Handle only the end of the tube that was placed into seal.

Place clean tube into the screwcap storage vial until used. Do not attempt to completely dry the tube. Do not smoke while cleaning the tubes or cones.

Ampule Analyzing Unit

- Replace magnesium perchlorate in primary drying tube whenever the lower section changes from dry solid to a semi-liquid, or when carrier gas flow is reduced.

- Take apart and clean the ampule breaking assembly by purging with water after breaking 30 ampules, or when carrier gas flow is reduced.

- Replace glass wool plug at breaking assembly outlet whenever necessary.

- Clean stainless steel purge tube by removing the plastic gas line and inserting a length of steel wire through the tube after breaking 30 ampules, or when carrier gas flow is reduced.

- Replace the silicone rubber seal on the purge tube in the ampule cutting plunger when the center hole in the seal becomes enlarged, or after analysis of several hundred ampules.

- Lubricate purge tube with silicone grease whenever necessary.